

Origin and palaeo-environmental significance of the Berrazales carbonate spring deposit, North of Gran Canaria Island, Spain

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ABSTRACT

The Berrazales carbonate spring deposit is a small outcrop constituted mainly by cascade-like geometries. Four main facies have been identified: *Fibrous dense macrocrystalline* formed by rapid degassing under high-flow conditions; *Framestones* of coated plant molds formed in moderate energy flow favoured by the presence of biogenic support; *Micrite/Microsparite* are primary precipitates in which crystalline aggregates nucleated on organic filaments and/or EPS; *Banded micrite-coarse crystalline* were the result of alternating physical-chemically and biologically induced precipitation in areas of varying flow-velocities. Most facies underwent different degrees of micritization processes. Micrite is distributed as thin lines penetrating the crystals, as irregular patches or as micrite layers. In the first case organic filaments penetrate crystals, suggesting that micritization is mainly biogenically driven. In the latter cases micritization is caused mostly by partial dissolution. Microbe participation in

micrite formation increased micrite MgCO_3 content in comparison with coarse crystalline facies.

Isotopic analyses show positive $\delta^{13}\text{C}$ values (+2.63 and +4.29‰ VPDB) and negative $\delta^{18}\text{O}$ (-5.65 and -4.48‰ VPDB) values. Positive $\delta^{13}\text{C}$ values clearly indicate fluids of thermal volcanogenic origin.

The Berrazales spring deposit studied here very probably is a small part of a larger carbonate building that was largely eroded by fluvial incision. Calculations of spring water temperature give a range from 20°C to 35°C, characteristic of a cold to warm spring favouring precipitation of calcite and important biogenic activity (*framestones*). Although the study deposit has textural characteristics of tufas, provide that the CO_2 sourced from deep fluids, it should be consider as thermogene travertine, being one more example of the difficulty of using those terms for ancient sedimentary deposits. Carbonate springs deposits, very rare in the Canary Islands, are good archives of recent volcanic activity, fluvial processes and vegetation regimes prevailing in the islands in recent times.

Keywords: carbonate spring deposit; travertine facies; Canary Islands; microbes; stable isotopes; volcanic setting.

1. Introduction

Calcareous spring deposits have been reported in various volcanic settings, such as in the hot-spot of Yellowstone (Fouke, 2011), in the Bogoria and Turkana lakes of the African Rift (Jones and Renaut, 1996; Renaut and Jones, 1997) and in arc-islands or compressive systems as in Japan (Nishiwaka et al., 2012). Other calcareous spring deposits are located along extensional fractures, such as the well-known Pamukkale-Karahayit travertines in Turkey (Hancock et al., 1999; Özkul, 2005), the Tivoli area (Gandin and Capezzuoli, 2014) or the Euganean geothermal field (Pola et al., 2014) in

Italy. The large hydrocarbon reservoir of the South-Atlantic Pre-salt also contains facies similar to carbonate spring deposits (Terra et al., 2010). In spite of increasing interest in the study of these deposits there is not yet a consensus on how to interpret many of their facies, nor on the role of biogenic versus abiogenic processes in their formation or on their classification (Ford and Pedley, 1996; Pentecost, 2005; Gandin and Capezzuoli, 2008; Gandin and Capezzuoli, 2014). Lack of consensus continues regarding calcareous spring deposits and also fluvial carbonates with regard to the use of terms travertine and tufa. Originally, travertine has been applied to compact rocks used for building construction material, whereas tufa usually denotes a softer more friable deposit (Viles and Pentecost, 2008). Even so, recently these terms have been scientifically redefined by some authors as Capezzuoli et al., (2014). Thus, travertine is defined for non-marine carbonates formed from hydrothermal-sourced waters, associated with tectonically active areas (and high geothermal heat flux) and characterized mainly by high depositional rates, low porosity, regular bedding and fine laminations, and an inorganic crystalline fabric. In contrast, the tufa is generally produced from meteoric water at ambient temperature and characterized by low depositional rates, high porosity and high content of microphytes and macrophytes (Capezzuoli et al., 2014, Table 1). Temperature of water feeding the spring is other classification criteria, although in cases it is difficult to apply to ancient deposits. Two main types of waters may feed springs: 1) organic CO₂-rich and low temperature waters (generally lower than 20°C) coming from the soil and groundwater form meteogene travertines, which have negative $\delta^{13}\text{C}$ (-12 to -2‰ PDB) values; 2) $\delta^{13}\text{C}$ values of thermogene travertines, sourced from hot to warm waters (generally higher than 30°C) coming from the interaction between host rock and CO₂ rich fluids at depth, vary between -2 to +10‰ PDB (Kele et al., 2011; Capezzuoli et al., 2014). Mineralogy, facies and microfacies of calcareous spring deposits are controlled by a set of environmental parameters such as: water chemical composition and temperature, rate CO₂ degassing, saturation levels and calcite deposition rate, macro and microbial

activity or the presence of some inhibitors (Talbot, 1990; Jones and Renaut, 2010; Guo and Chafetz, 2014; Sun et al., 2014). This makes spring deposits good palaeo-environmental archives (Andrews, 2006; Anzalone et al., 2007; Keppel et al., 2012; Gradziński et al., 2013; Gradziński et al., 2014).

In the Canary Islands carbonate spring deposits are very scarce (Demény et al., 2010, Alonso-Zarza et al., 2012; Rodríguez-Berriguete, 2012). In this paper we study the Berrazales spring deposit, located in Gran Canaria Island. Our aims are to unravel: a) the thermal-volcanic influence in the formation of carbonate spring deposits in volcanic settings, b) the role of biogenic versus abiogenic processes and their interrelation during and after crystalline growth and, c) water physicochemical conditions (temperature, pH, chemistry, etc.) controlling the formation of the deposits. Our conclusions can be an aid to the understanding of the processes and the main controls involved in the formation of travertines in volcanic settings and their palaeo-environmental and palaeo-hydrological significance.

2. Geographical and geological setting

The Canary Islands (Spain) are located off the NW African coast, between 29° 25' and 27° 37' N and 18° 10' and 13° 20' W, developed over the Jurassic oceanic lithosphere as a result of the eastward movement of the African plate over a mantle hotspot (Holik et al., 1991; Carracedo et al., 1998; Carracedo et al., 2002). Similar to other intra-plate volcanic islands, the Canarian archipelago displays the hotspot volcanic stages of evolution: juvenile (shield), volcanic quiescence and rejuvenated stage. Gran Canaria, actually in an advanced rejuvenated stage, is a nearly circular island located at the centre of the Canarian archipelago. A dense radial network of deep ravines ("barrancos", the local toponymy) dissects the island, forming a rugged topography. The sub-aerial development of Gran Canaria records a juvenile stage (ca. 14.5–8.0 Ma), a volcanic quiescent stage (ca. 8.0–5.5 Ma) and a rejuvenated stage (ca. 5.5 Ma

to present) including the Roque Nublo stratovolcano and the Post-Roque Nublo volcanism (Pérez-Torrado et al., 1995; Carracedo et al., 2002; Guillou et al., 2004; Aulinas et al., 2010). The most recent Post-Roque Nublo volcanism, Holocene in age, created a monogenetic volcanic field with at least 24 vents. The eruptive style is mainly strombolian with formation of small scoria cones and lava flows, mostly with aa morphologies (Rodríguez-González et al., 2009; Rodríguez-González et al., 2012). The Holocene vulcanism has a strong control on the development of the few carbonate spring deposits have been studied in Gran Canaria. One of these deposit is Azuaje travertine described by Rodríguez-Berriguete et al. (2012) located 9 km north-east of the study area.

The carbonate deposits studied are located above the stratigraphic contact between scoria cone and lava flow of the Berrazales eruption (Fig. 1A), in the upper part of Barranco Los Ríos (Fig. 1B). The lava flow is classified as basanite (Rodríguez-González et al., 2009). Holocene lava flows were emplaced at the bottom of the ravines, with little erosive incision and draining towards the coast (Rodríguez-González et al., 2009; Rodríguez-González et al., 2012). This eruption is stratigraphically related with Jabalobos (dated by ^{14}C at $2,760 \pm 60$ BP) and Fagajesto (dated by ^{14}C at $3,030 \pm 90$ BP) eruptions (Rodríguez-González et al., 2009; Aulinas et al., 2010).

3. Methods

Samples of the Berrazales outcrop were studied using conventional petrological, mineralogical and geochemical analyses. Twenty six samples were chosen for conventional optical petrographic study in thin sections. Fragile thin sections were impregnated with epoxy resin.

Mineralogical semi-quantitative composition of all samples was determined by X-ray powder diffraction (XRD) using a Philips PW-1710 with $\text{CuK}\alpha$ at 40 KV and 30 mA.

MgCO₃ mole percent is measured from d-spacing of calcite crystal lattice, which was determined by the variation of 2 θ value of the principal calcite peak of the X-ray diffractograms (Goldsmith et al., 1961; Tucker, 1988; Scholle and Ulmer-Scholle, 2003; Ries et al., 2008).

The texture and components studied in 12 gold-coated samples were determined using a JEOL JSM 6400 scanning electron microscope on the Research Support Centre (CAI) of Geological Techniques of UCM (Madrid, Spain), working at 20kV with a resolution of 35Å. Secondary electron and backscattering detectors were used together with an X-ray detector system to obtain semi-quantitative compositions. For the study it was also necessary to use a FEI INSPECT (5350 NE Dawson Creek Drive Hillsboro, Oregon 97124, USA) of the Museo Nacional de Ciencias Naturales (Madrid, Spain), operating with high vacuum mode (0.08 to 0.60 torr) with conductive samples to be studied with both the large field detector (LFD) and backscatter detector (BSED-detector electron backscatter). SEM resolution at high vacuum was 3.0 nm at 30 kV (SE), 10 nm at 3 kV (SE), and 4.0 nm at 30 kV (BSE). The accelerating voltage was 20-30 kV, high vacuum 0.45 torr, working distance of 10 mm.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from 21 selected powdered samples were analysed at the Scientific and Technical Survey in Barcelona University (Spain). Samples were obtained with a drill and reacted with 100% phosphoric acid at 70°C for 3 minutes. CO₂ was extracted using a Thermo Finnigan Carbonate Kiel Device III isotopic analyzer with a Thermo Finnigan MAT-252 spectrometer, according to the McCrea (1950) method. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, corrected using the NBS-19 standard and with an analytical precision of $\pm 0.02\text{‰}$ for $\delta^{13}\text{C}$ and 0.03‰ for $\delta^{18}\text{O}$, are expressed in parts per thousand (‰) referred to VPDB standard.

4. Results

4.1. Outcrop features of the Berrazales carbonate deposit

Berrazales carbonate deposit is a small outcrop approximately 6-7 m long, located between volcanic cinder cones and Holocene lava materials. The outcrop has three sectors: the eastern sector consists of cascade morphologies dipping to the east; the western sector dips to the west; in the central sector the cascades are vertical. In the eastern side the cascade geometries include large molds of tree trunks, one with a diameter larger than 50 cm.

Individual carbonate cascade bodies, of a maximum height of 3 m and width of about 0.5-1.5 m, are composed of various vertical to oblique irregular centimeter-thick beds (Fig. 2A, B).

4.2. Facies and microfacies: description and interpretation

4.2.1. Fibrous dense macrocrystalline facies

Description

Fibrous dense macrocrystalline facies, 1.5-2.0 cm thick bands of fibrous pale calcite crystals, 1.0-1.5 cm long and length-width ratio >10:1 (Fig. 3A) have intercalations of micritic and more porous laminae. Fibrous crystals nucleate and grow on sub-horizontal surfaces or on plant molds and have branching feather or dendrite morphologies (Jones and Kahle, 1986; Jones and Kahle, 1993; Guo and Riding, 1992; Jones et al., 2000; Kele et al., 2011). Sometimes feather or dendritic crystals appear growing from a small filament (>300 µm long and around 12 µm thick) (Janssen et al., 1999; Gradziński, 2010) (Fig. 3B). Thin light-brown laminae (2-15 µm thick) are included within the feather crystals. Also brownish-black darker laminae (10-15 µm thick) separate dendritic crystalline bands (Fig. 3A). Above those laminae there are

small inclusions of triangular microsparite crystals inside large fibrous crystals (Freytet and Verrecchia, 1999). Both light-brown and brownish-black sheets are curved and acquire the upper surface morphology of dendrites. Terminations of fibrous crystals are micritized (Fig. 3C, D) by microbes. Microbial filaments also penetrate coarse crystals generating microborings (Fig. 3D, E) and parallel tubular porosity (Fig. 3F).

Interpretation

These crystalline facies appear to be the product of rapid precipitation from supersaturated water with respect to calcite due to rapid CO₂ degassing under disequilibrium conditions (Jones et al., 2005). In particular, calcite branching feathers or dendrites have been described in areas of rapid growth (Jones and Kahle, 1986) due to high-flow conditions (~2 m/s) (Okumura et al., 2012) favouring rapid CO₂ loss. Thin light-brown laminae alternating within feathers are the result of temporal variations in precipitation, probably caused by rhythmic increases-decreases in diverse atomic element content, such as Fe, probably reflecting recurrent annual growth cycles (Jones et al., 2005; Jones and Renaut, 2008). Brownish-black laminae indicate stages of interrupted crystal feather growth, due to variations in water geochemistry (presence of undersaturated waters, low flow rates, microbial activity, etc.). Even so, the presence of organic matter as the origin for brownish-black laminae cannot be ruled out, as described by Freytet and Verrecchia (1999). Connected circular microborings are due to the activity of microbes, such as cyanobacteria (Radtke and Golubic, 2011; Okumura et al., 2012) or fungi (Calvet, 1982; Golubic et al., 2005) which penetrate, dissolve and micritize calcite crystals.

4.2.2. Framestone facies

Description

Framestone is a porous macrocrystalline facies mostly composed of subparallel coated plant molds 1-3 cm long and 0.5-8 mm in diameter (Fig. 4A). As in *fibrous dense macrocrystalline* facies, small fibrous crystals (<3 mm long) are arranged perpendicular to molds, forming fans (~3 mm) and including thin light-brown lamination (2-15 µm thick) (Fig. 4B). The top surfaces of fans are covered by a dark-brown irregular micritic mass (<0.2 mm thick). Micrite is also distributed between large fibrous crystals. Note that plants molds have also well-defined parallel structure (Fig. 4C).

Interpretation

Vegetal molds provided nuclei for the precipitation of crystalline fans. Similar but larger fans described on Pancura Pitu's travertine (Centra Java, Indonesia) by Okumura et al. (2012) were interpreted as having been precipitated under fast-flow conditions (~2 m/s). In our case flow velocities were probably lower than 2 m/s, as indicated by the smaller size of fans and by the presence of plant molds, whose preservation would have been inhibited under very high energy water (Okumura et al., 2012). Dark-brown micritic masses are formed by the breakdown of coarse calcite crystals by abiogenic or biogenic processes (Kobluk and Risk, 1977; Calvet, 1982; Jones and Kahle, 1995; Martín-García et al., 2009). Even so, lack of biogenic features, such as filaments or cyanobacterial microborings, suggest that dark micrite masses were formed by abiogenic processes.

4.2.3. Micrite-coarse banded crystalline facies

Description

Micrite-coarse banded crystalline facies consist of palisade calcite crystals (up to 1 mm long) sub-perpendicular to substrate. Crystals include very thin (2-10 µm) reddish-translucent microlaminae and dark-micritic laminae (Fig. 4D). Reddish-translucent

microlaminae are laterally very uniform and regular whereas dark-micritic ones are more irregular. V-shaped morphologies of both laminae are governed by the morphology of crystal edges. Sometimes the laminae penetrate crystal edges. Dark micritic laminae are amalgamated and contain very small filaments (<0.1 mm long) in contact with the external surface.

Interpretation

The lack of any biogenic features in the palisadic crystals suggests that purely physicochemical processes mainly governed crystal formation (Riding, 2008). The thin reddish translucent microlaminae are similar to those described in the afore-mentioned *fibrous dense macrocrystalline* facies, indicating cyclic changes in chemical, physical and/or environmental conditions (Valero-Garcés et al., 2001) or even diurnal cycles of microbial activities (Okumura et al., 2013a; Okumura et al., 2013b). Dark micritic laminae within the palisade crystals are probably formed when calcite crystals come into contact with undersaturated fluids with respect to CaCO₃ (Jones and Kahle, 1995) as also described in coarse crystalline speleothems (Martín-García et al., 2009), or due to the presence of very small concentrations of organic matter (Pedley, 1992; Gradziński, 2010). Small filaments on external surfaces suggest that biological micritization of those dark-micritic laminae cannot be ruled out.

4.2.4. Micrite/Microsparitic facies

Description

Micrite (<4 µm) / *Microsparitic* (4-100 µm) facies are either homogeneous or banded. Homogeneous microfacies are composed of micrite/microsparitic masses which include crystalline aggregates of pale calcite crystals, arranged on thin organic filaments (~700 µm long and <10 µm thick). Transversally, these aggregates have

spherulitic morphologies (Fig. 5A). Banded microfacies consist of an alternation of: a) Microsparitic bands containing crystalline fans (~500 µm) (Fig. 5B); b) Dendrolitic fabric (Perri et al., 2012) composed of filamentous cyanobacteria (500-800 µm long) arranged vertically and calcified by sparite crystals (around 100-200 µm long) (Fig. 5C, D) with a length-width ratio of 3:1; c) Dark micritic layers around 0.2 mm thick; d) Irregular porous sheets (>0.5 mm thick) with semi-circular pores (0.5 mm to 1.5 cm across), making the rock significantly porous. Some pores are filled by light-translucent bladed sparitic crystals (around 100 µm long and 25 µm thick) arranged as gravitational, meniscus and also as isopachous cements. These facies also contain not-mineralized exopolymeric substances (EPS) (Fig. 5E, F) from microbial activity.

Interpretation

Lack of dissolution features of crystalline aggregates and absence of any primary fabric substitution suggest that micrite/microsparite is a primary precipitate. Crystalline aggregates probably nucleated on organic filaments which provided a site for calcium carbonate nucleation (Pentecost, 2005). Several studies have linked the formation of similar spherulites with microbial activity, which generated a favourable microenvironment for Ca^{2+} and Mg^{2+} concentration and calcium carbonate precipitation (Castanier et al., 1989; Buczynski and Chafetz, 1991). Similar processes led to both the formation of crystalline fans, as the result of initial calcite nucleation on biogenic structures within the micrite, and subsequent growth by purely physicochemical processes (CO_2 degassing, evaporation...) (Jones and Renaut, 2010). However, organic nuclei are not always preserved (Guo and Riding, 1992), because bacteria and cyanobacteria may be completely destroyed within hours by crystal growth (Krumbein et al., 1977).

Dark micritic layers probably represent the precipitation of micrite on extracellular polymeric substances (EPS) (Chacón et al., 2006) in association with cyanobacteria

and biological processes (Perri et al., 2012). EPS can be partially decomposed by aerobic heterotrophic bacteria, inducing CaCO₃ precipitation (Dupraz et al., 2004; Gautret et al., 2004; Decho et al., 2005). The result is the calcification of the EPS biofilm by micritic crystals (Turner and Jones, 2005; Okumura et al., 2013b).

Irregular porous sheets may result from dissolution of micrite precipitated on EPS or from organic matter degradation (Perri et al., 2012). Gravitational and meniscus cements consist of bladed crystals, suggesting that samples were subject to both vadose and phreatic post-depositional processes.

4.3. Diagenetic features

The main diagenetic processes that influence the final aspect of Berrazales travertine are micritization, dissolution and cementation.

Micritization consists of partial or total substitution of coarse calcite crystals by a mass of micritic/microsparitic calcite crystals (2-15 µm). There are two types of micritization. The first type affected some specific bands and the topmost fibrous feather crystals of *fibrous dense macrocrystalline* facies. Bands less than 1 cm thick are composed of irregular micrite patches alternating with non-micritized fibrous calcite crystals (Fig. 6A). Besides, tops of fibrous feather and dendrite crystals are also perforated by a biogenic network (Fig. 6B) composed of thin microbial filaments (Fig. 6C), suggesting a biogenic origin for micritization (Radtke and Golubic, 2011; Okumura et al., 2012). Microspar is considered an intermediate product between coarse calcite and micrite.

The second type of micritization consists of thin micritic laminae (2-15 µm) separating large crystal formations, mainly in *micrite-coarse banded crystalline* facies and in *fibrous dense macrocrystalline* facies. Lack of biogenic features in *framestone* facies and the fact that micrite does not penetrate in large crystals suggests that micrite formation is due to inorganic physicochemical changes, probably caused by

undersaturated water inflow or variations in environmental conditions (Jones and Kahle, 1995; Martín-García et al., 2009).

Dissolution processes also play an important role in micritic/microsparitic samples, forming irregular and non-continuous, fenestral-like porosities. Dissolution may be due to undersaturated calcite water input (Martín-García et al., 2009) and/or due to the degradation of microbial organic matter.

Cements occur in *micrite/microsparitic* facies either as bladed calcite crystals (80-150 μm long) covering the whole surface of the pore or as meniscus and gravitational cements, indicating that cementation occurred in both vadose and phreatic environments.

4.4. Mineralogy and isotope geochemistry

Samples are mainly (proportions higher than 95%) composed of Low Magnesium Calcite (LMC) along with minor traces of phyllosilicates (< 5%). Content of MgCO_3 in most samples varies between 2% and 5%, except in sample BER-17 which has two calcite peaks corresponding to two calcite phases with 4% and 11% in moles of MgCO_3 (Table 1). In general, higher Mg contents (4-11% in moles of MgCO_3) are in *micrite/microsparitic* facies. Macrocrystalline facies (*fibrous dense macrocrystalline* facies and *framestone* facies) contain between 0% and 3% in moles of MgCO_3 whereas *micrite-coarse banded crystalline* facies lack magnesium (Table 1).

Isotopic values obtained from different facies show only slight variations in $\delta^{13}\text{C}$ and in $\delta^{18}\text{O}$, probably due to the small size of the outcrop and absence of fractionation between water and mineral phase (HCO_3^-). All samples have positive (+2.63 and +4.29‰ VPDB) $\delta^{13}\text{C}$ and negative (-5.65 and -4.48‰ VPDB) $\delta^{18}\text{O}$ values (Fig. 7A, B), with a correlation coefficient of 0.59. The lightest values of $\delta^{18}\text{O}$ correspond to the macrocrystalline samples while heaviest ones are found in micritic facies, which are

also enriched in Mg. Some micritized bands in macrocrystalline facies show an increase in $\delta^{18}\text{O}$ relative to non-micritized ones. Changes between different facies in $\delta^{13}\text{C}$ show smaller variations.

5. Discussion

5.1. Facies types, biogenic versus abiogenic processes and palaeo-environmental setting

The small Berrazales deposit, one of the few carbonate deposits found in Gran Canaria Island, outcrops in Los Rios Valley, formed after the last volcanic event around 2,700 – 3,100 years ago, surely in relation with volcanic eruptions occurred in Jabalobos and Fagajesto (Fig. 1A). Its exceptional situation on a recent lava flow deposit, along with its cascade morphology, strongly suggests formation from spring waters, similar to nearby Azuaje travertine (Rodríguez-Berriguete et al., 2012).

Facies indicate different conditions for calcite precipitation. *Fibrous dense macrocrystalline* facies precipitated during rapid CO_2 degassing (Jones et al., 2005), favouring the rapid growth of fibrous branching feather or dendrite crystals (Jones and Kahle, 1986; Okumura et al., 2012). Vegetal molds, stems and microbial filaments act as support and nuclei for calcite precipitation. In *framestone* facies, the absence of reworking and preservation of molds in live position suggest that water-flow velocity was not higher than <2 m/s (Okumura et al., 2012), allowing growth and later calcification of vegetal molds. In contrast, primary micrite precipitated in a calm water environment highly saturated in CaCO_3 (Jones and Kahle, 1995).

It is difficult in these deposits to distinguish the role of biogenic from abiogenic processes in the formation of the various facies. In most cases both processes acted together. For example, the formation of fibrous feather crystals faithfully reflects the interaction of biogenic and abiogenic processes and denote changing of crystallization

rates of calcite. In a first stage, microbial filaments (Fig. 8A) act as templates for small calcite crystal (up to 100 μm long) nucleation (Fig. 3B; Fig. 5A, C, D; Fig. 8B). Organic filaments provided a favourable site for calcite nucleation (Pentecost, 2005; Gradziński, 2010) and a good microenvironment for Ca^{2+} and Mg^{2+} concentration (Castanier et al., 1989; Buczynski and Chafetz, 1991), although the slow crystal growth allows filaments not to be completely entombed. In contrast, during a second stage, crystallization rate is too fast for microbial community and physicochemical precipitation prevails. Thus, the rapid growth of calcite, principally due to the rapid abiogenic CO_2 degassing, enables the development of large branching feathers or dendrites (Fig. 3A; Fig. 8C). In a final stage, large fibrous crystals are infected by microbes (fungi or cyanobacteria) (Fig. 3E and Fig. 6C), which penetrate them causing partial micritization (Fig. 3C, D; Fig. 6A, B; Fig. 8D) (Radtke and Golubic, 2011; Okumura et al., 2012). These microbial colonization indicate a diminishing growth rate of crystals or their completely cessation. On the contrary, *framestone* facies underwent abiogenic micritization by dissolution caused by undersaturated water inflow (Fig. 4B) (Jones and Kahle, 1995; Martín-García et al., 2009).

A more clearly biogenic influence is seen in the formation of micrite/microsparite with higher MgCO_3 due to the replacement of exopolymeric substances (EPS) by high magnesium calcite (HMC) (Dupraz et al., 2004; Dupraz and Visscher, 2005). The degradation of EPS by heterotrophic bacteria (Decho et al, 2005) liberates Ca^{+2} , Mg^{+2} and HCO_3^- which were bound to EPS, increasing cation concentration in solution and allowing micritic Mg-calcite precipitation (Dupraz et al., 2004, Okumura et al., 2013a).

5.2 Discussion of stable isotope data

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in continental carbonate deposits are mainly controlled by the isotopic composition of water, temperature of formation, pH of the solution, calcite deposition rate, saturation degree, diagenesis, microbial activity, evaporation, CO_2

outgassing and fractionation between water and mineral phase (Talbot, 1990; Valero-Garcés et al., 2001; Dietzel et al., 2009; Guo and Chafetz, 2014; Sun et al., 2014).

Positive $\delta^{13}\text{C}$ values indicate “deep-source” fluids in relation with volcanic activity or decarbonation (Pentecost, 2005). Considering the volcanic area of the study, $\delta^{13}\text{C}$ positive values of Berrazales may suggest that this continental deposit was precipitated from thermal waters which were saturated with heavy CO_2 from bedrock (Özkul et al., 2014), influenced by significant contribution of volcanic-hydrothermal CO_2 . Carbonate spring deposits precipitated from heavy hydrothermal CO_2 waters, have typical values ranging between -2 and +10‰ PDB (Pentecost, 1995; Pentecost, 2005; Viles and Pentecost, 2008). The Berrazales deposit is in this range, with similar $\delta^{13}\text{C}$ values to the Azuaje travertine described by Rodríguez-Berriguete et al. (2012) and to other travertines of the world (Fig. 9). These deposits can be classified as thermogene deposits following Pentecost (2005) classification. $\delta^{13}\text{C}$ values in hot-water travertine deposits are mainly controlled by physical (CO_2 degassing or water temperature) and microbial processes (Kele et al., 2008; García-del-Cura et al., 2014). On the other hand, changes in $\delta^{18}\text{O}$ values can also reflect the effect of evaporation, temperature of water and, at the time of precipitation, degassing of CO_2 and/or groundwater inflow (Chafetz and Lawrence, 1994; Valero-Garcés et al., 2001; Kele et al., 2008). In Berrazales deposit changes in evaporation, water temperature or degassing were probably not significant because the small size of the deposit did not allow water to re-equilibrate. CO_2 removal and subsequent variations in $\delta^{13}\text{C}$ values in Berrazales travertine could occur due to biological processes, such as respiration or microbial photosynthesis (García-del-Cura et al., 2014). Microbes consumed preferably the lighter carbon isotope, enriching water and the precipitated calcite in the heaviest isotope, as shown by heavy $\delta^{13}\text{C}$ values and high Mg content on micrite/microsparite, precipitated under the influence of EPS.

A temperature of 23°C of the water of the abandoned spa, placed 570 m downflow of the Berrazales deposit (Garraalda-Iribarren, 1952) and the $\delta^{18}\text{O}$ values of the crystalline

crust (sample BER-11) were used to obtain the possible original $\delta^{18}\text{O}$ signal of the water precipitating this crust. A value of -3.33‰ V-SMOW was obtained for equilibrium precipitation using Kim and O'Neil (1997) equation, whereas the value for disequilibrium conditions, obtained through Halas and Wolacewicz, (1982) equation, according to Kele et al. (2011), was 5.5‰ V-SMOW. These values, which are in the range of the reported from Gran Canaria Island, -2 to -6‰ , (Gonfiantini et al, 1976; Gasparini et al., 1990), were used to calculate the probable temperature of precipitation of the other facies of the deposit (Table 2A, B).

Temperatures obtained under equilibrium conditions and $\delta^{18}\text{O}_w = -5.5\text{‰}$ (9.4 to 14.8°C) are very low compared to reported groundwater temperatures for Gran Canaria Island of 14 - 35°C (Gonfiantini et al., 1976; Custodio et al., 1987; Gasparini et al., 1990). The later are similar to temperature calculations under disequilibrium (19.7 - 35.4°C) and fit well with the measured value of 23°C (Garraalda-Iribarren, 1952). Cooling trends in surface needed to pass from, at least, 23°C (at spring) to 9°C (downflow) are also highly improbable at this altitude on Gran Canaria Island, suggesting that if calcite precipitated from waters with $\delta^{18}\text{O}_w = -5.5\text{‰}$ (or slightly higher values) at about 23°C , it occurred under disequilibrium conditions (Table 2B). The relatively narrow values of temperatures obtained for the different facies indicate that the probable vent (crystalline crust) and cascade deposits (the other facies) were very near as shown by the small size of the Berrazales outcrop. However, these calculations may be not that precise as desirable, as for example there may be ^{18}O isotope shift effects and temperature could have changed along the life of the spring.

$\delta^{13}\text{C}$ value from the same sample has been used to obtain the original signal of $\delta^{13}\text{CCO}_2$ (Table 3). The values obtained using Mook et al. (1974) $\text{HCO}_3^- - \text{CO}_2(\text{g})$ equilibrium equation (used here for disequilibrium precipitation) are similar to those of fluids derived from tectono-metamorphic processes (Hoefs, 1997; Minissale, 2004). However, they are in the range of those reported in literature as volcanic originated fluids from Canary Islands, which are usually higher than -4‰ (Albert et al., 1986;

Custodio et al., 1987; Gasparini et al., 1990). The calculated values using Bottinga (1968) and Panichi and Tongiorgi (1976) equations (Table 3) fit well with the typical range of volcanic CO₂, -5 to -7‰ PDB (Hoefs, 1997), which are slightly lighter than those of the volcanic CO₂. Therefore, only deep source for CO₂ can be invoked here through isotopic calculations, and no precisions between tectono-metamorphic derived or volcanic derived CO₂ can be assessed. However, giving the overall setting, the CO₂ was probably of volcanic origin.

6. Conclusions

The Berrazales carbonate building is characterized mainly by cascade morphologies, with different types of facies, such as (1) *Fibrous dense macrocrystalline facies*, (2) *Framestone facies*, (3) *Micrite/microsparitic facies* and (4) *Micrite-coarse banded crystalline facies*. Fibrous feather or dendrite crystals grew from the interaction between biogenic and abiogenic processes, starting from crystalline nucleation on microbial filaments to the last phase of rapid physicochemical crystal growth (CO₂ degassing) under rapid water flow and disequilibrium conditions. In *Framestone facies*, presence of parallel plant molds suggests that water energy could not be very high (<2 m/s), preserving plants apparently in live positions. On the contrary, primary micrite precipitated during lower flow and calmer waters probably in relation with EPS. Finally, the thin banded facies indicate chemical, physical or environmental changes during carbonate precipitation. Micritization processes are also under both biogenic (crystal perforations by microbial filaments) and abiogenic (undersaturated water inflow, changes in environmental conditions) processes.

Calcite is the principal mineral making up the travertine, generally with low Mg contents, except micritic samples formed from microbial activities and EPS formation.

Positive $\delta^{13}\text{C}$ values (+2.63 and +4.29‰ VPDB) found in thermogene travertines indicate formation from “deep source” fluids, in this volcanic area probably related with thermal waters and volcanic activity. Whereas, negative $\delta^{18}\text{O}$ values (-5.65 and -4.48‰ VPDB) reflect a meteoric water signal. Thus, temperatures calculated (20-35°C), heavy $\delta^{13}\text{C}$ values and the situation of the Berrazales deposit indicate that the CO_2 was very probably of thermal origin and sourced from or below the Earth’s crust.

As are other thermogene spring deposits in Gran Canaria, Berrazales carbonate deposit is an excellent example of the interplay between volcanic and sedimentary processes, due to its location on previous volcanic materials deposited 2,700 – 3,100 years ago. The described deposit is a particular case study of a carbonate spring which from the textural point of view can be classified as tufa (meteoene travertine) but from the geochemical point of view ($\delta^{13}\text{C}$) as travertine (thermogene travertine).

The study of the Berrazales deposit has provided valuable information about thermal water temperature, volcanic CO_2 contribution to thermal water springs, the role of abiogenic versus biogenic processes in its formation and the presence of fresh water streams in the island. At present very few examples of carbonate springs have been described in the Canary Islands as their preservation in erosive regimes of volcanic settings is exceptional.

7. Acknowledgements

We acknowledge A. Meléndez, M.C. Cabrera and J.F. Pérez-Torrado for his assistance during the field work. James Cerne reviewed the English version of the manuscript. Special thanks for Xabi Arroyo from CAI of Geological Techniques of UCM and to the reviewers, Michal Gradziński and anonymous one, for their suggestions and comments. This research was funded by Project CGL-2011-27826-CO2-01 from MINECO.

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502 **8. References**

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772

773 **Figure captions**

774

775 **Fig. 1.** (A) Location of the Berrazales area, in the north-west of Gran Canaria Island.
776 (B) Situation of the Berrazales Carbonate Deposit (BCD) between volcanic materials in
777 the Barranco Los Ríos.

778

779 **Fig. 2.** (A) Photograph of the main part of Berrazales deposit. (B) Sketch from
780 Photograph A, showing the dominance of cascade facies and location of the samples.
781 Two molds of trunks can be observed (red arrows). The carbonate deposits overlie the
782 volcanic lava.

783

784 **Fig. 3.** Photographs of *Fibrous dense macrocrystalline* facies. (A) Fibrous feather or
785 dendrite crystals separated by dark micritic laminae. (B) Microbial filaments (arrows)
786 encased within feather dendrite crystals. (C) Tops of crystalline feathers are micritized
787 (arrows). (D) Detailed view of the red rectangle of C, showing microbial filaments
788 penetrating large crystals and generating circular microborings (arrow). (E) SEM image
789 of circular microbial filament microborings. (F) SEM image showing parallel porosity
790 created by penetration of a network of microbial filaments.

791

792 **Fig. 4.** (A) *Framestone* facies composed of parallel plant molds coated with calcite. (B)
793 Plant mold surrounded by coarse calcite crystals. (C) SEM image showing parallel
794 structure of plants molds. (D) *Micrite-coarse crystalline banded* facies with reddish-
795 translucent (1) and dark-micritic (2) laminae. Arrows show V-shaped morphologies,
796 located between the edges of palisade crystals.

798 **Fig.5.** Photographs of *Micrite/microsparitic* facies. (A) Crystalline microsparitic
 799 aggregates growing from organic filaments within a micritic mass. (B) Microsparitic
 800 band composed of crystalline fans in a porous micritic mass. (C) Dendrolitic fabric
 801 composed of calcified cyanobacterial filaments. (D) SEM image of a calcified filament
 802 in transverse view. Arrow indicates the central hole left by dissolved filament. (E)
 803 Exopolymeric substances (EPS) (arrows) intercalated within calcite crystals and
 804 cyanobacterial filaments (f). (F) Detail of EPS (arrows).

805

806 **Fig. 6.** (A) Calcite crystals penetrated by a network of microbes. (B) Fibrous feather
 807 calcite crystals intercalated with altered micritic masses. (C) Detail of calcite crystals
 808 penetrated and altered by thin microbial filaments (arrows).

809

810 **Fig. 7.** Stable carbon and oxygen isotope composition of Berrazales carbonate deposit
 811 samples according to: (A) facies and (B) Mg content.

812

813 **Fig. 8.** Growth phases of fibrous branching feather or dendrite morphologies. (A)
 814 Microbial filament. (B) Sparite nucleating on biogenic support. (C) Abiogenic growth of
 815 fibrous calcite crystals. (D) Perforation and micritization of fibrous calcite by microbes
 816 (cyanobacteria or fungi).

817

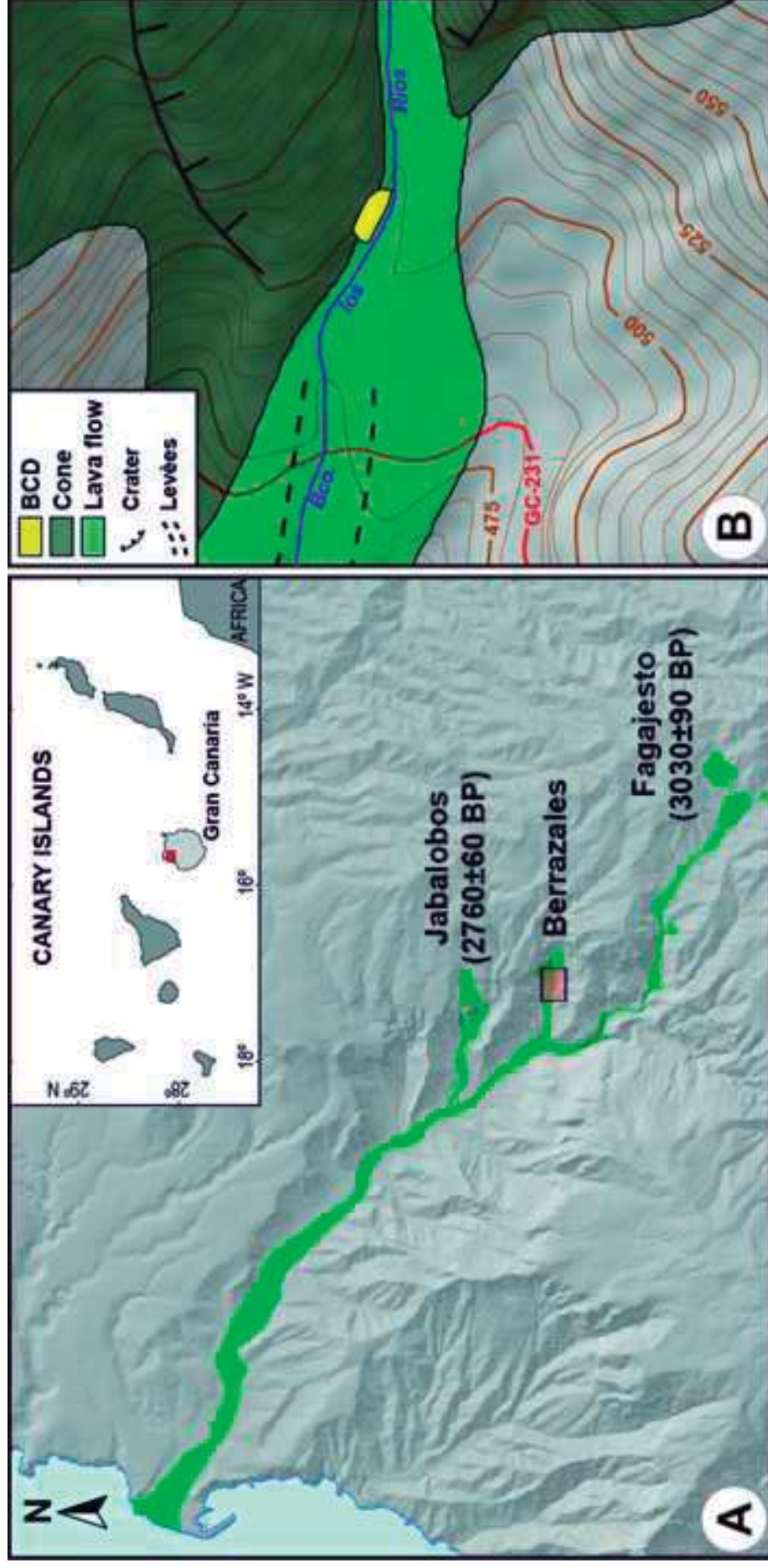
818 **Fig. 9.** Stable isotope composition of some travertines and tufas from the world
 819 including the data from this study.

820

Table 1. Berrazales carbonate deposit samples: type of facies; mineralogy; principal calcite peak with the respective content of MgCO_3 ; and stable isotope composition.

Table 2. Calculations of: $\delta^{18}\text{O}_{\text{calcite}}$ (‰, VSMOW); $\delta^{18}\text{O}_{\text{water}}$ (‰, VSMOW); $\Delta\text{HCO}_3\text{--H}_2\text{O}$; and Temperature under disequilibrium and equilibrium conditions. (A) Calculated with $\delta^{18}\text{O}_{\text{water}} = -3.33\text{‰}$ VSMOW. (B) Calculated with $\delta^{18}\text{O}_{\text{water}} = -5.50\text{‰}$ VSMOW.

Table 3. Calculation of the original $\delta^{13}\text{CCO}_2$ from calculated temperatures of the crystalline crust (BER-11) (see temperature in disequilibrium from Table 2A, B). $\delta^{13}\text{CCO}_2$ is calculated with equations of Mook et al. (1974), Panichi and Tongiorgi (1976), and Bottinga (1968).



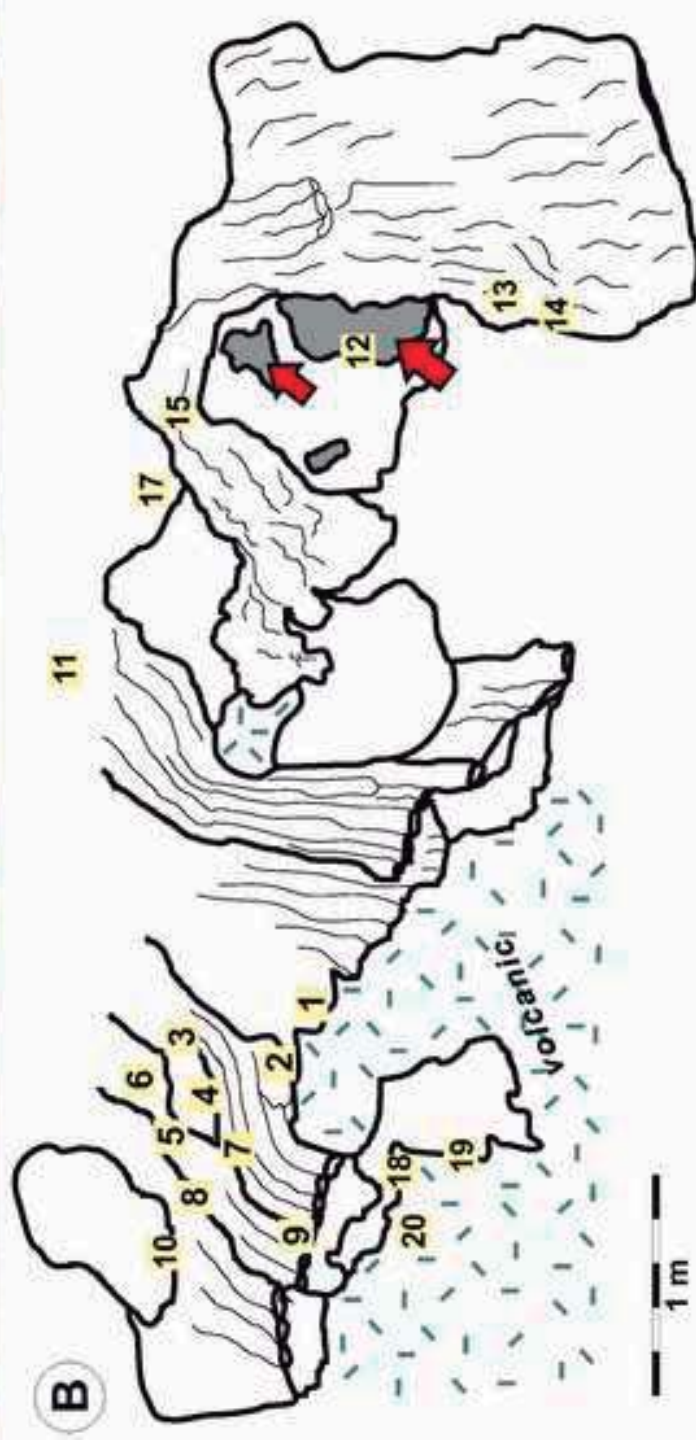
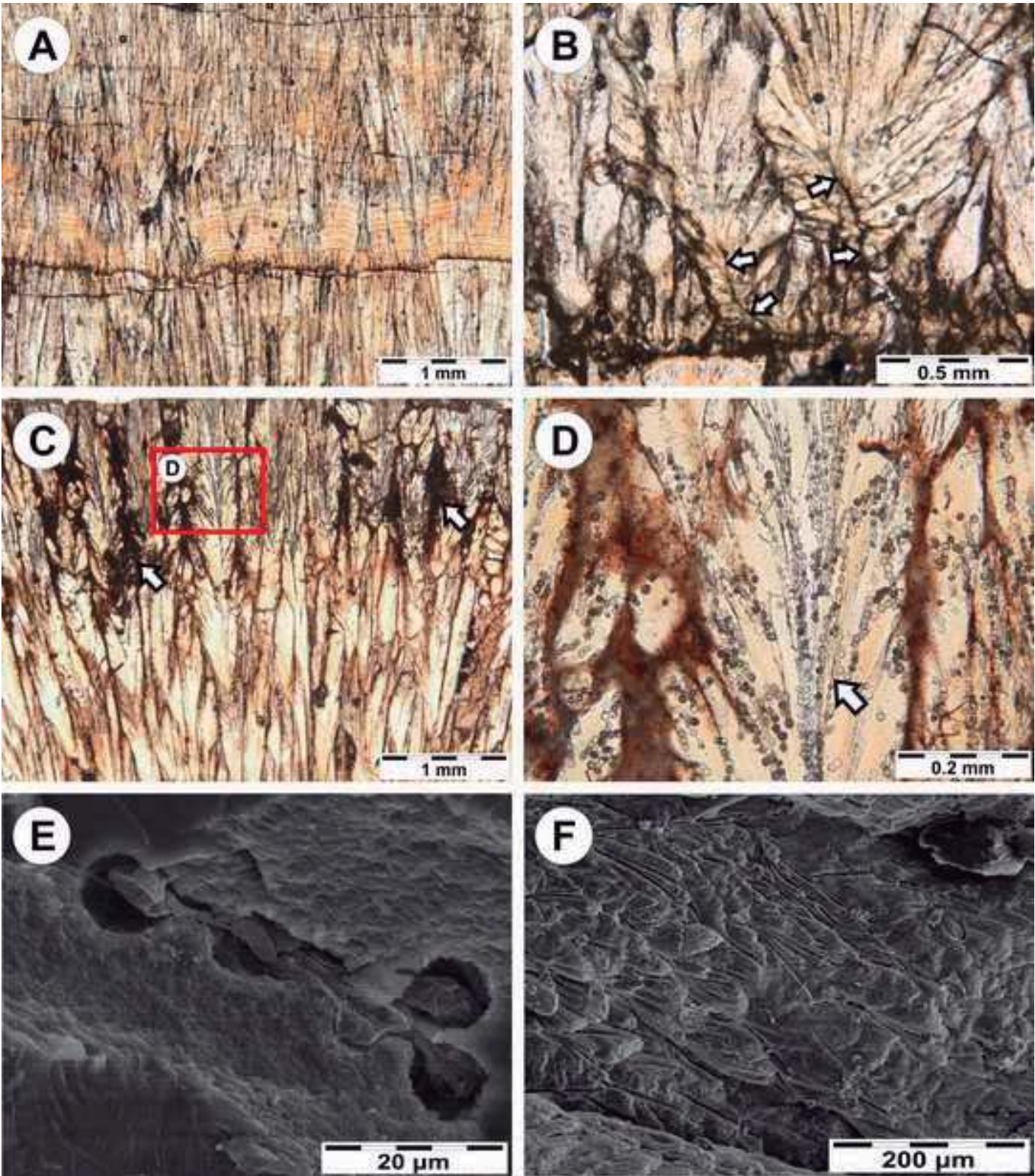


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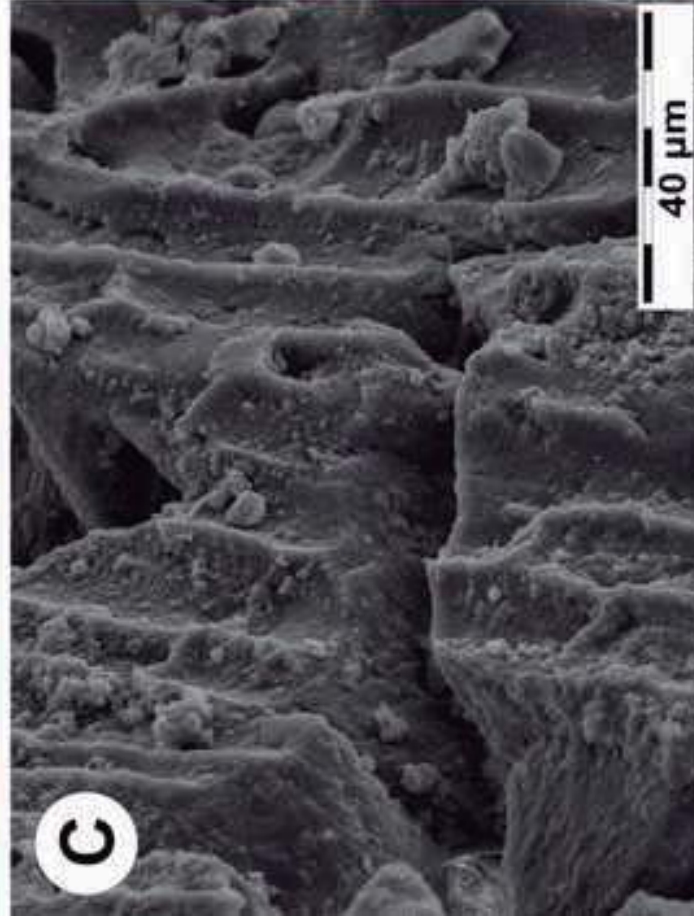
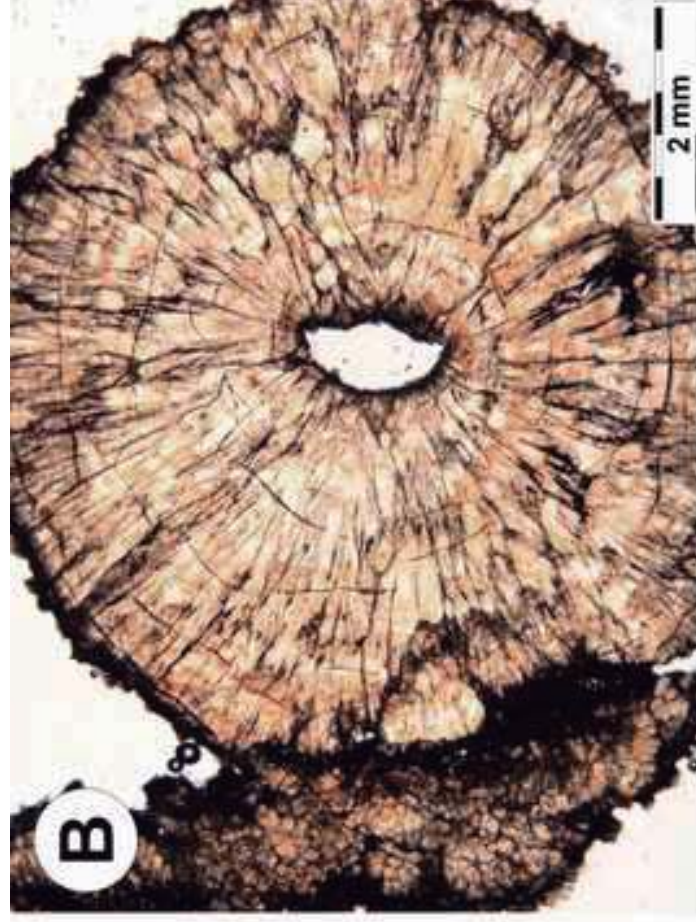


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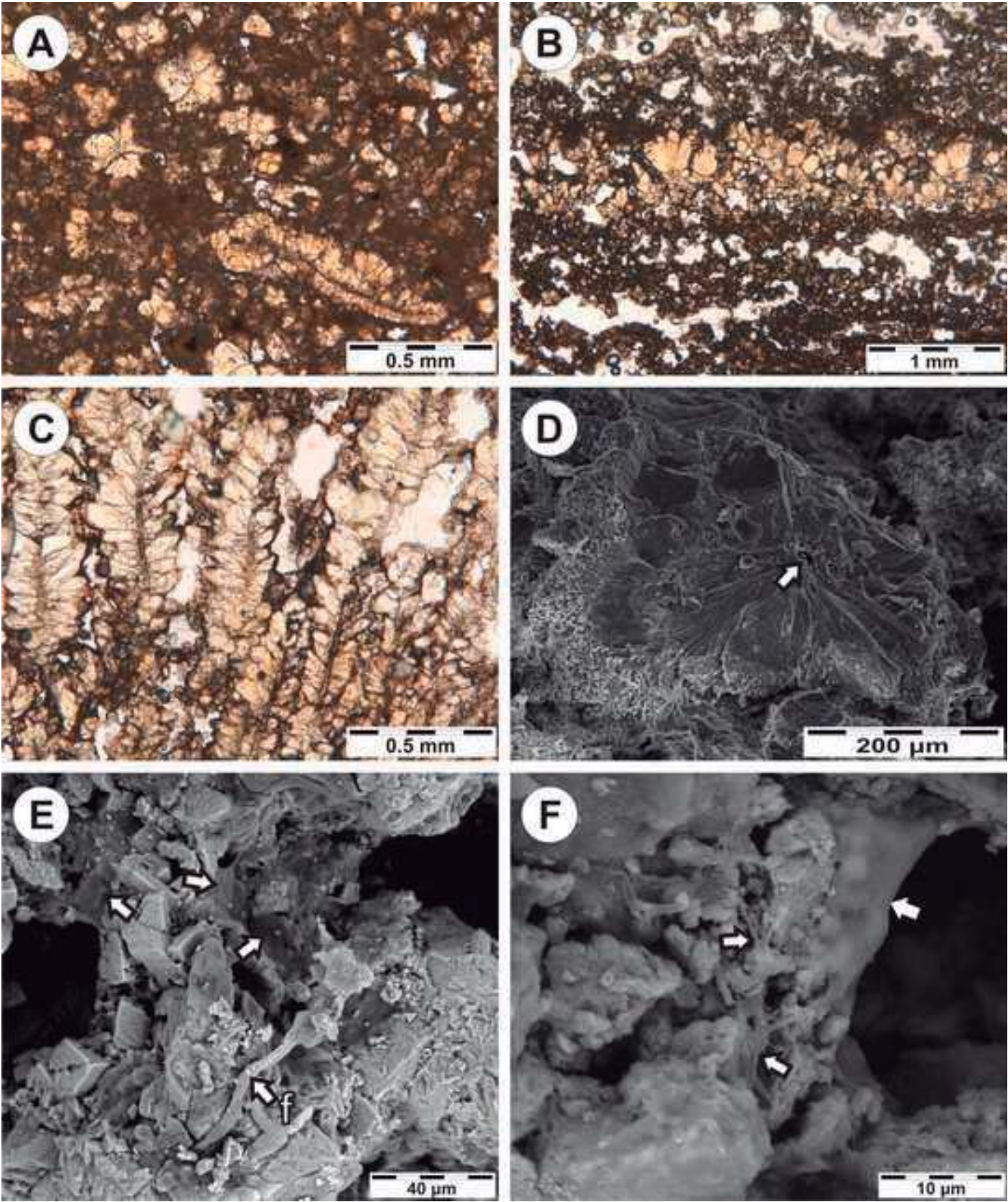
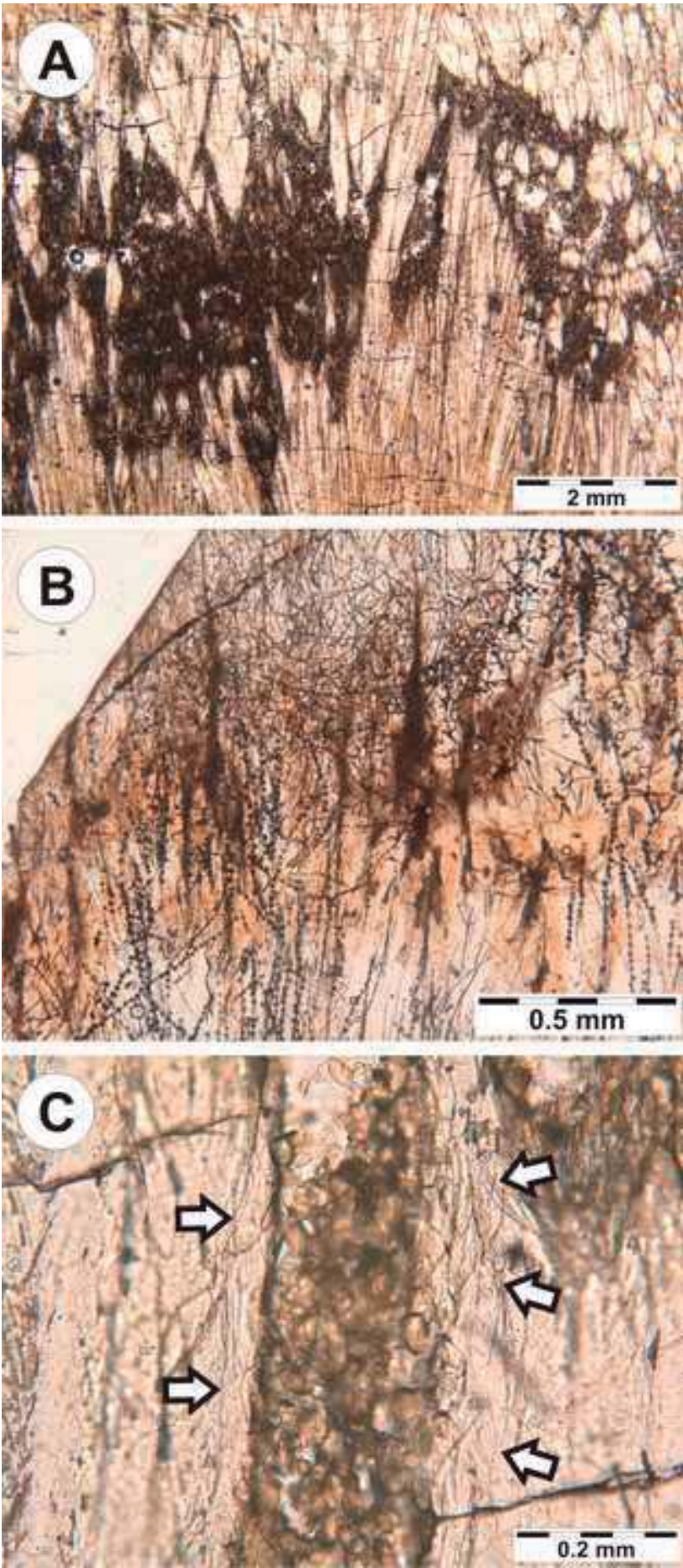
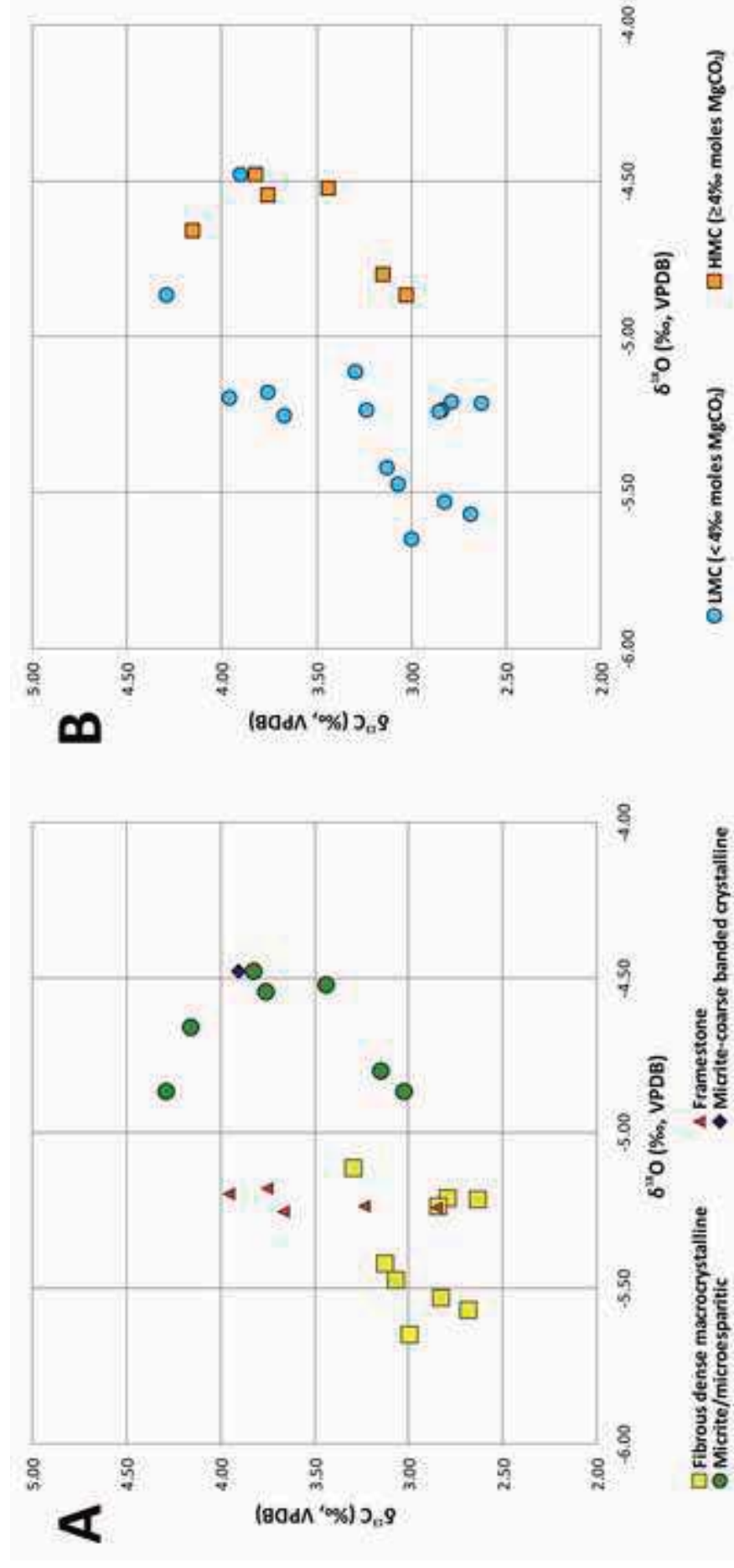


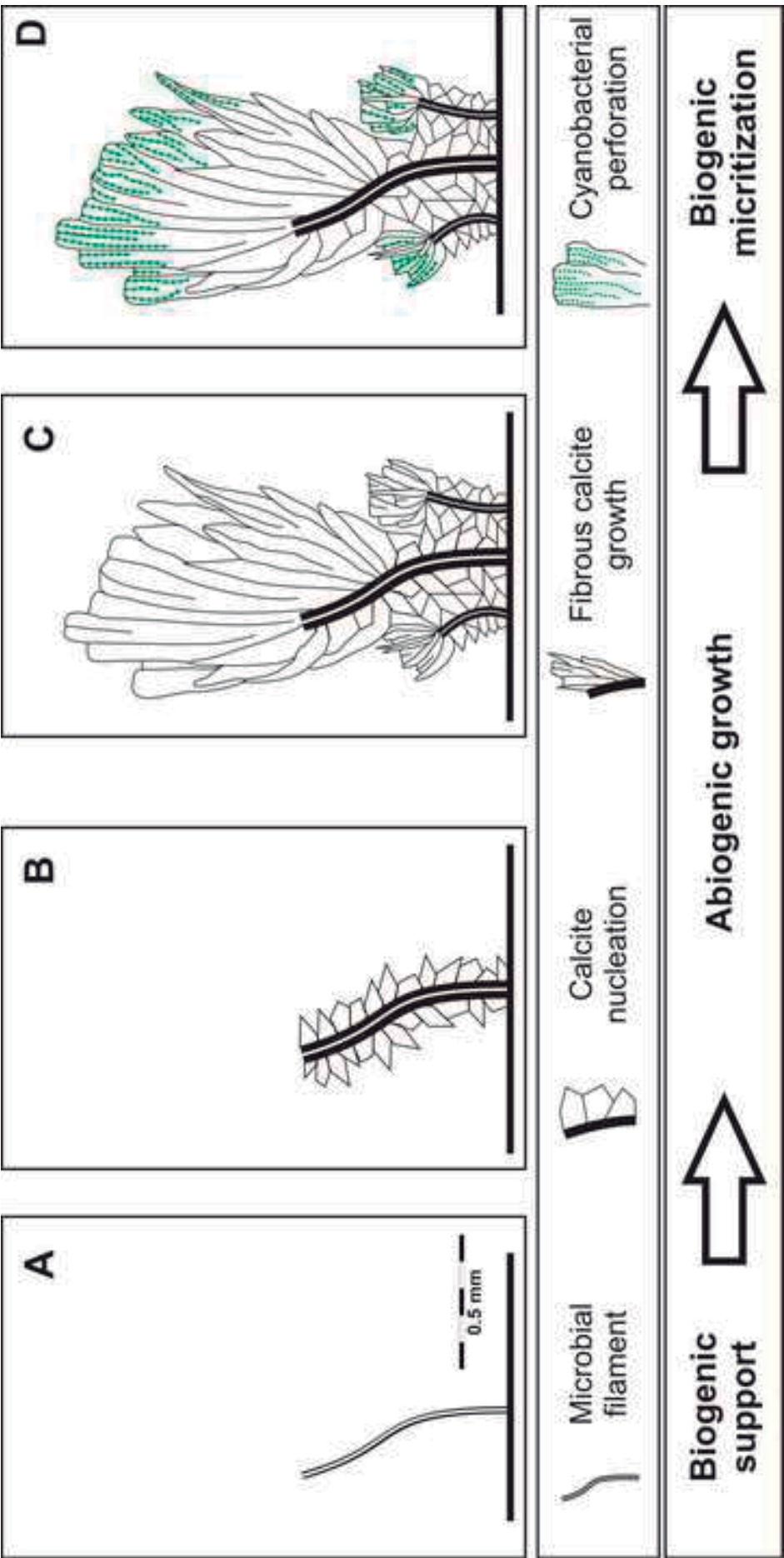
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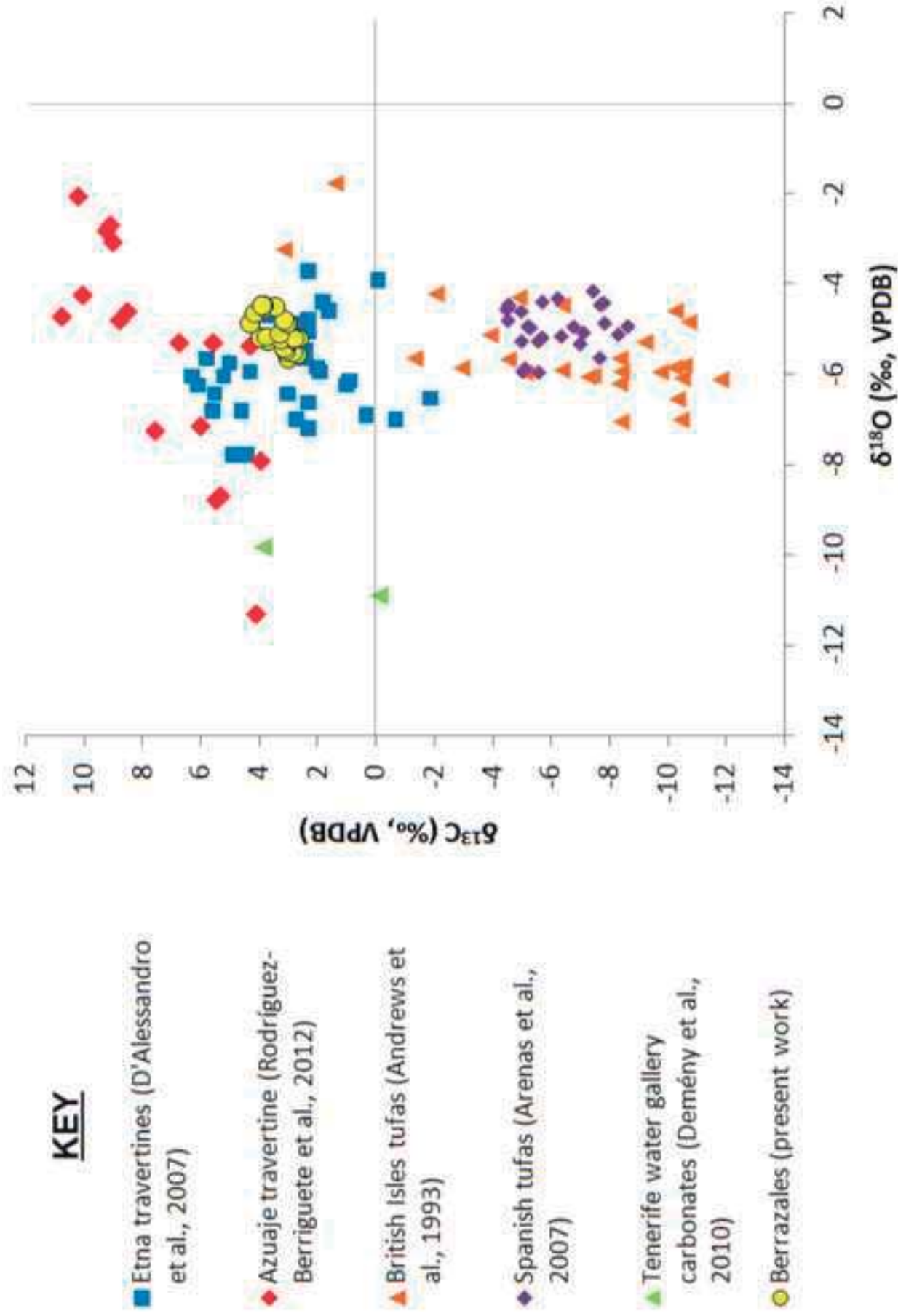




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Sample	Type of Facies	Mineralogy (Semi-quantitative)		Principal calcite peak (°2θ)	% Moles MgCO ₃	δ ¹³ C _{calcite} (‰, VPDB)	δ ¹⁸ O _{calcite} (‰, VPDB)
		% Calcite	% Phyllosilicates				
BER-1	Framestone	100	*	29.16	0	3.67	-5.25
BER-2	Micrite-microsparitic	100	*	29.58	5	3.15	-4.80
BER-3	Fibrous dense macrocrystalline	100	*	29.46	2	2.83	-5.53
BER-3.1	Fibrous dense macrocrystalline	100	*	29.48	2	2.63	-5.21
BER-4	Fibrous dense macrocrystalline	100	*	29.48	2	2.69	-5.57
BER-5	Fibrous dense macrocrystalline	100	*	29.46	2	3.00	-5.65
BER-6	Framestone	100	*	29.46	2	3.24	-5.23
BER-7	Fibrous dense macrocrystalline	100	*	29.48	2	3.07	-5.47
BER-8	Micrite-microsparitic	90	10	29.54	4	3.82	-4.48
BER-9	Fibrous dense macrocrystalline	100	*	29.48	2	3.30	-5.11
BER-10	Fibrous dense macrocrystalline	100	*	29.44	2	3.12	-5.42
BER-11	Fibrous dense macrocrystalline	100	*	29.45	2	2.79	-5.21
BER-11.1	Fibrous dense macrocrystalline	100	*	29.45	2	2.84	-5.24
BER-12	Micrite-microsparitic	90	10	29.5	3	4.29	-4.86
BER-13	Framestone	100	*	29.5	3	3.96	-5.20
BER-14	Framestone	100	*	29.48	2	3.75	-5.18
BER-15	Micrite-microsparitic	100	*	29.57	5	4.15	-4.66
BER-17	Micrite-microsparitic	100	*	29.54 - 29.77	4 - 11	3.76	-4.55
BER-18	Framestone	100	*	29.46	2	2.85	-5.24
BER-18.1	Micrite-microsparitic	100	*	29.54	4	3.03	-4.87
BER-19	Micrite-microsparitic	100	*	29.58	5	3.44	-4.52
BER-20	Micrite-coarse banded crystalline	100	*	29.31	0	3.90	-4.48

Asterisks (*) indicate that the proportion of phyllosilicates is below 5%

Table 2A

Sample	$\delta^{18}\text{O}_{\text{calcite}}$ (‰ VSMOW)	$\Delta\text{HCO}_3^- - \text{H}_2\text{O}$	T diseq.(°C) ⁽¹⁾	T eq.(°C) ⁽²⁾
BER-1	25.13	28.46	33.3	23.2
BER-2	25.59	28.92	31.1	20.9
BER-3	24.84	28.17	34.8	24.6
BER-3.1	25.17	28.50	33.1	23.0
BER-4	24.80	28.13	34.9	24.8
BER-5	24.72	28.05	35.4	25.2
BER-6	25.15	28.48	33.2	23.1
BER-7	24.90	28.23	34.5	24.3
BER-8	25.92	29.25	29.5	19.4
BER-9	25.27	28.60	32.6	22.5
BER-10	24.96	28.29	34.2	24.0
BER-11	25.17	28.50	33.1	23.0
BER-11.1	25.14	28.47	33.3	23.1
BER-12	25.53	28.86	31.4	21.2
BER-13	25.19	28.52	33.0	22.9
BER-14	25.20	28.53	33.0	22.8
BER-15	25.74	29.07	30.4	20.2
BER-17	25.85	29.18	29.8	19.7
BER-18	25.14	28.47	33.3	23.1
BER-18.1	25.53	28.86	31.4	21.2
BER-19	25.88	29.21	29.7	19.6
BER-20	25.92	29.25	29.5	19.3

⁽¹⁾ $10^3 \ln a (\text{HCO}_3^- - \text{H}_2\text{O})_{\text{eq.}} \approx 10^3 \ln a (\text{CaCO}_3 - \text{H}_2\text{O})_{\text{diseq.}} = 2.92 \times 10^6 / T^2 - 2.66$ (Halas and Wolacewicz, 1982)

⁽²⁾ $10^3 \ln a (\text{CaCO}_3 - \text{H}_2\text{O}) = 18.03 \times 10^3 / T - 32.42$ (Kim and O'Neil, 1997)

Table 2B

$\delta^{18}\text{O}_{\text{calcite}}$ (‰ VSMOW)	$\Delta\text{HCO}_3^- - \text{H}_2\text{O}$	T diseq.(°C) ⁽¹⁾	T eq.(°C) ⁽²⁾
25.13	30.63	23.2	13.0
25.59	31.09	21.1	10.9
24.84	30.34	24.5	14.3
25.17	30.67	23.0	12.8
24.80	30.30	24.6	14.5
24.72	30.22	25.0	14.8
25.15	30.65	23.1	12.9
24.90	30.40	24.2	14.0
25.92	31.42	19.7	9.4
25.27	30.77	22.5	12.3
24.96	30.46	23.9	13.8
25.17	30.67	23.0	12.8
25.14	30.64	23.1	12.9
25.53	31.03	21.4	11.2
25.19	30.69	22.9	12.7
25.20	30.70	22.8	12.6
25.74	31.24	20.5	10.2
25.85	31.35	20.0	9.7
25.14	30.64	23.1	12.9
25.53	31.03	21.4	11.2
25.88	31.38	19.9	9.6
25.92	31.42	19.7	9.4

Table

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Author	Equation	Temperature (°C)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰, VPDB)
Mook et al. (1974)	$10^3 \ln \alpha (\text{HCO}_3^- - \text{CO}_2(\text{g})) = 9.552 \times (10^3/T) - 24.1$	33	-4.31
		23	-5.38
Panichi and Tongiorgi (1976)	$\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = 1.2 \times \delta^{13}\text{C}_c - 10.5$	independent	-7.15
Bottinga (1968)	$10^3 \ln \alpha_c = -2.4912 + (7.663 \times 10^3/T) - (2.9880 \times 10^6/T^2)$	33	-6.58
		23	-7.95